

# RECENT RESULTS ON THE KINETICS OF COAL PYROLYSIS AND HYDROPYROLYSIS AND THEIR RELATIONSHIP TO COAL STRUCTURE

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## 1. Introduction

Pyrolysis of coal is understood to be its thermal decomposition at temperatures beyond 300 °C, whereby gas, tar and char are formed. It is the basic process of coking and the starting reaction of combustion, gasification and hydrogenation. In addition the application of pyrolysis offers the possibility to convert coal into gases and liquids in a "third way" besides gasification and hydrogenation. Thereby the yield of volatile matter can be substantially increased by hydrogen at high pressures - "hydro-pyrolysis".

For all these reasons coal pyrolysis has been and is being studied worldwide by many scientists. Recent reviews are owed to Howard /1/ and Gavalas /2/. For some 20 years scientists at Bergbau-Forschung have been carrying out systematic studies on the kinetics and mechanism of pyrolysis /3-8/. In continuation of this work, during the last few years, in the frame of the IEA pyrolysis project the influence of ambient gas atmosphere and pressure on course and products of coal pyrolysis have been investigated extensively /9-11/. Within this scope special interest was laid also on the formation kinetics of the single compounds of the BTX aromatics during pyrolysis and hydro-pyrolysis /12/. This contribution reviews in brief our main results on course, products, kinetics and mechanism of pyrolysis reactions on coal. Moreover it deals with a first attempt to establish a link between these findings and the most recent results on the chemical constitution of coal /13/.

## 2. Experimental Techniques and Basic Results

To cover a wide range of heating rates by the laboratory work different types of equipment have been used /9/. The results presented in this paper are mainly measured in a thermobalance, in which approximately 1 g of a coal sample can be heated up with some °C/min in a gas stream at pressures up to 100 bar in a temperature range between 20 and 1.000 °C. The progress of the reaction is measured by the weight loss and by the continuous analysis of the gaseous reaction products. Some additional results are presented at high heating rates, which have been achieved using the grid heater technique, whereby about 10 mg of finely ground coal are pyrolysed on a electrically heated wire mesh net. Most of the experimental results presented in this paper are measured taking coals from the Ruhr area. Here they are characterized in short by their volatile matter content (V.M.). The complete data can be found elsewhere /8,9,10/.

A characteristic result using the thermobalance is given in fig. 1, showing the formation rates of the main products. The mass loss depicts the overall reaction and thereby the formation of the char and occurs in two steps. The volatile matter - tar and gaseous products - are liberated in one or a few single reactions for each component. Fig. 2 shows the gas formation for a wide rank of German coal. In all cases - with the exception of CO<sub>2</sub> and the hydrogen (not given in the figure) - the curves show a systematic degradation by coalification of those groups, which have a weaker bonding and are therefore liberated at lower temperature during pyrolysis.

Course of product formation and yields are controlled by chemical reaction on the one hand and transport phenomena inside the particle on the other. The latter gains in influence, if particle diameter, heating rate and pressure increase. An example for quantitative measurements and relevant calculations is given in fig. 3. As a function of particle diameter and heating rate a curve has been established separating areas where - depending on diameter and heating rate - transport phenomena or chemical reaction controls the overall process. With higher pressure it is shifted to lower values for diameter and heating rate. The region, in which the chemical reaction is rate determining, meets to a high degree the conditions in technical reactors regarding pressure, particle size and rate of heating. Thus kinetics themselves are not influenced by transport processes, however by the different residence times of the product inside the particle secondary reactions may control yields. This is especially true for the liquid volatile matter as can be seen by the formation of the tar and - as an example of the BTX aromatics - the benzene (fig. 5), whereby pressure favours obviously the cracking of the liquids. This is true for the whole rank /10/. Fig. 7 gives quantitative data for two rates of heating. However, by comparison of low and high heating rate the latter exhibits a higher yield of liquids as the residence time of the products inside the particle is considerably smaller.

The effect of hydrogen exists mainly in an increase of the formation of liquid products, which are now formed in a two reactions (fig. 6). The peak between 350 and about 480 °C is slightly affected mainly by the influence of the pressure as discussed before and can be ascribed to pyrolysis. However with rising pressures the second reaction becomes more and more important. The enhancing influence of hydrogen pressure on the yield of tar as well as on BTX aromatics is demonstrated in fig. 9 for three different high volatile coals. It is remarkable that up to 40 % of the coal can be converted into liquids ultimately at 100 bar under low heating rates. The BTX aromatics have a share of about 10 % of the total tar. Fig. 10 summarizes results of the characterization of tar samples, taken at different temperatures during hydropyrolysis. It shows that the concentration of the aromatics in the tar increases with rising temperature and that the BTX aromatics are mainly formed at the end of the tar formation. The second reaction of tar formation mainly can be ascribed to hydrogenation and the formation of the BTX to hydrocracking.

### 3. Kinetics and Mechanism

A derivation of mathematical equations to describe product formation curves for coal pyrolysis is given in fig. 9, left side. They have been achieved under the assumption that the rate of the formation of a particular product is dependent on the concentration of functional groups in the coal, the degradation of which results in this product /3/. With these equations the measured curves can be described excellently as the examples on the right hand

side of fig. 9 confirm. This is also true for  $\text{CH}_4$  in which formation 2 to 3 reactions participate. The values for the kinetic parameters found for these four examples depending on pressure are listed in table 1. In a similar way also the formation of other gases like  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and of tar and BTX aromatics during hydropyrolysis have been formally described and the relevant kinetic parameters have been published /12/.

The peak for tar formation can be described best by a first order reaction. Aliphates with more than two C-atoms show a curve of a simple structure, which has been described under the assumption of a reaction order of  $n=1$  and a distribution of E and  $k_0$  /6,8/. The support for this assumption is that the rupture of bondings is rate determining and the bonding energies are distributed because of the interactions with different neighbour groups. However, as shown in fig. 9, also  $n=2$  together with distinct values for E and  $k_0$  formally give an excellent description of the reaction peaks. It can be interpreted by interactions of the radicals formed in the primary step. Moreover it has formal advantages in a subsequent mathematical treatment e.g., when modelling reactors. In the same way also the curves for methane can be described under the assumption of several reactions either each with distributed E and  $k_0$ -values or under the assumption of  $n=2$  with distinct E and  $k_0$ .

The ideas about the mechanism of the product formation as mentioned before are schematically given in fig. 10. The most relevant steps are thermal activation, breaking of chemical bonds and formation of stable molecules by reactions of the radicals. The total process can be described by a first order law, when the slow step (II) is rate determining. A second order law makes sense, when the step IIIc controls the overall reaction. On the whole it can be stated that the kinetic equations and the conditions concerning E and  $k_0$  are based on assumptions, which are most compatible with possible reaction models. It follows that an extrapolation of the results, achieved with the relevant mathematical methods can be performed with a high degree of confidence. It should be mentioned that the release of  $\text{H}_2$ , being extremely wide spread over the temperature range, can only be interpreted by an overlap of many first order reactions resulting in a broad distribution of E and  $k_0$  due to the fact the C-H-bonding energies in the coal molecule are also extremely widely distributed.

#### 4. Chemical Constitution of Coal and Kinetics of Pyrolysis

Fig. 11 gives the model molecule for a high volatile bituminous coal (83 % C) /14/. The most recent analytic diagnoses for determining both the functional CH- and  $\text{CH}_2$ -groups by NMR spectrometry as well as the functional oxygen-containing groups, entered the model. It also reflects the chemical reactions having been observed with coal. From general knowledge on bonding energies in organic molecules it can be derived, that the C-C-bonding energies at the bridges between ring systems are much weaker than those of other C-C-bonds, particularly in the aromatic structures. Thus it may be expected, that cracking of the coal molecule between the different ring systems will be a first step of coal degradation during pyrolysis being possible already at moderate temperature of about 400 °C.

Following conclusions may, therefore, be drawn when looking at the coal constitution and the kinetics of pyrolysis: the begin of tar formation at 350 °C can be assumed by the distillation and diffusion of smaller organic molecules (molecular weight below 150 - 200) having been trapped in the quite narrow pore structure of the coal. Parallel thermal degradation of the coal molecule

takes place at temperatures at about 400 °C according to the primary reaction steps as given schematically in fig. 10. The reactions commence at 400 °C by cracking of the bridge-carbons which have the lowest bonding energies and as a consequence by dissociating of the aromatic ring units whereby radicals are formed. Due to fast recombining reactions among the smaller radicals and their reactions with hydrogen, formation of small aliphatic gas molecules, like CH<sub>4</sub> and H<sub>2</sub>O takes place. Also bigger ring fragments become hydrogen-saturated and distillate as tar with medium molecular weight. This explains the simultaneous occurrence of tar CH<sub>4</sub>, C<sub>2</sub>-, C<sub>3</sub>-hydrocarbons, and water above 400 °C. Also formation of coke will commence via condensation of the ring systems, under elimination of hydrogen which appears for the first time in gaseous form above 420 °C. At high temperatures there will finally be produced also CO by cracking of heterocyclic oxygen groups.

The above mechanisms are backed up by the carbon-, hydrogen-, and oxygen-balances both for the pyrolysis products as well as for the functional groups of the coal molecule /13/. The same mechanism basically applies also to high pressures and heating rates. The effect of high pressure consists, inter alia, in a shifting of tar formation towards higher temperatures due to a shifting in the boiling range so that at the expense of the tar yield the parallel coke-generating condensation will be intensified. The elementary hydrogen liberated under high pressures will beyond 700 °C lead to an increased methane yield due to a partially hydro-gasification of carbon. High heating rates will result in a faster disengagement of the tar and thus reduce the proportion of condensing reactions.

If hydrogen is present the reaction mechanisms of coal pyrolysis change substantially, under additional formation of tar, aromatic compounds (fig. 6, 7, 8) and CH<sub>4</sub> at the expense of coke. This may be explained by the fact that beyond 500 °C, concurrently to the cracking, recombining and condensation reactions as explained, there occurs partial hydrogenation of aromatic systems which are then subject to hydrocracking. This reaction helps to increase volatile matter and reduces coke formation. The mechanism of such hydrocracking depends on whether interior or exterior aromatic rings have been hydrogenated. In the first case formation of diphenyl (under separation of methane) may occur. In the second case polynuclear aromates with aliphatic lateral chains will in a first place be formed which are decomposed partially under elimination of methane. This may be plausible explanation for the increased formation of tars, BTX aromates and methane. The additional water formation observed can be explained by hydrocracking of ether groups.

## Conclusion

To sum up: Kinetic data have been evaluated to describe the formation rates of the most important products of coal pyrolysis. Also the yields depending on pressure and heating rates are well-known. Both kinetic parameters and yields have been measured covering the whole rank of hard coal. Moreover the most important liquid products evolved during hydropyrolysis can be described in the same manner. These data are now available and utilized for the modelling of pyrolysis reactors and those processes, in which pyrolysis plays an important role, like combustion, hydrogenation and fixed bed gasification. In addition the recent findings on the molecular structure of coal have lead to a detailed understanding of the single steps during pyrolysis and hydropyrolysis, thereby proving the formal kinetic approaches and showing new ways process optimisation.

## References

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pressure bar		1		100	
		E	$k_o$	E	$k_o$
tar	$n = 1$	138	$7.6 \cdot 10^8$	174	$1.5 \cdot 10^{11}$
benzene	1) $n = 1$	140	$2.1 \cdot 10^{11}$	136	$2.0 \cdot 10^{11}$
	2) $n = 2$	142	$6.0 \cdot 10^7$	115	$2.0 \cdot 10^6$
	3) $n = 2$	150	$1.0 \cdot 10^7$	149	$8.0 \cdot 10^6$
$CH_4$	1) $n = 2$	204	$7.8 \cdot 10^{11}$	214	$7.8 \cdot 10^{11}$
	2) $n = 2$	158	$2.7 \cdot 10^7$	141	$5.3 \cdot 10^5$
	3) $n = 2$	-	-	257	$1.8 \cdot 10^{11}$
$C_2H_6$	$n = 2$	210	$1.5 \cdot 10^{13}$	224	$2.2 \cdot 10^{13}$
$C_2H_4$	$n = 2$	205	$2.7 \cdot 10^{13}$	218	$7.1 \cdot 10^{13}$

E in kJ/mol;  $k_o$  for  $n = 1$  in l/min;  $k_o$  for  $n = 2$  in  $g/cm^3$  min.

Table 1: Values for kinetic parameters for the curves given in fig. 9 (right side)

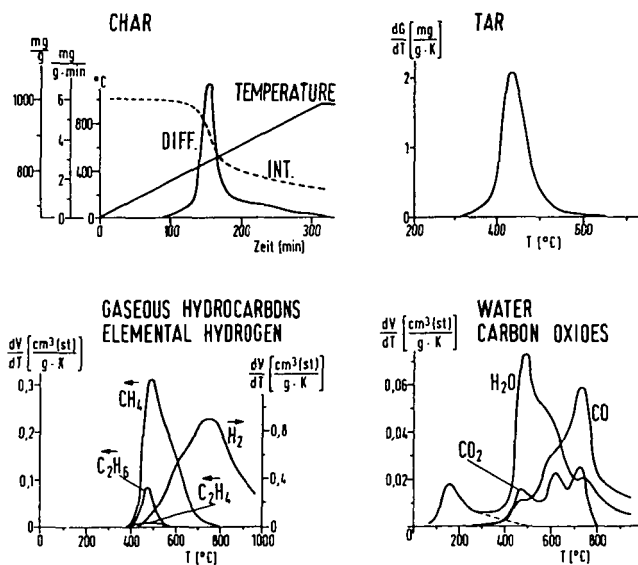


Fig. 1: Example for the product formation during pyrolysis of a German coal (32 % V.M. daf); heating rate: 3 K/min; atmosphere:  $N_2$ ; total pressure: 11 bar)

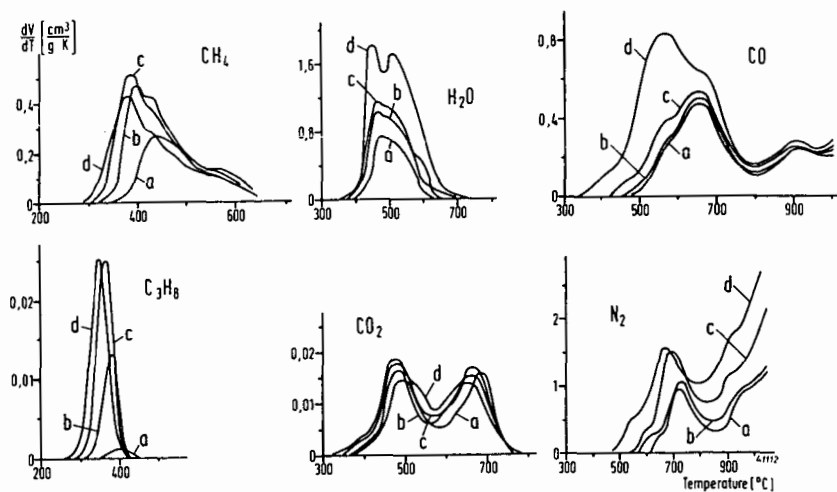


Fig. 2: Formation of the main pyrolysis gases for coals of different rank  
(coal a: 10 % V.M.; b: 19,5 %; c: 29 %, d: 39,5 %)

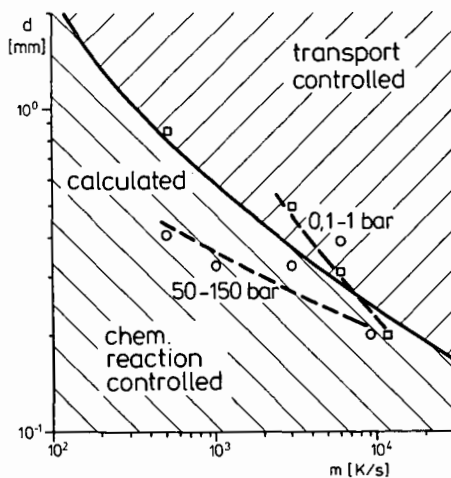


Fig. 3: Influence of particle diameter ( $d$ ), heating rate ( $m$ ) and pressure on the rate determining step of the pyrolysis for a German h.v. bit. coal

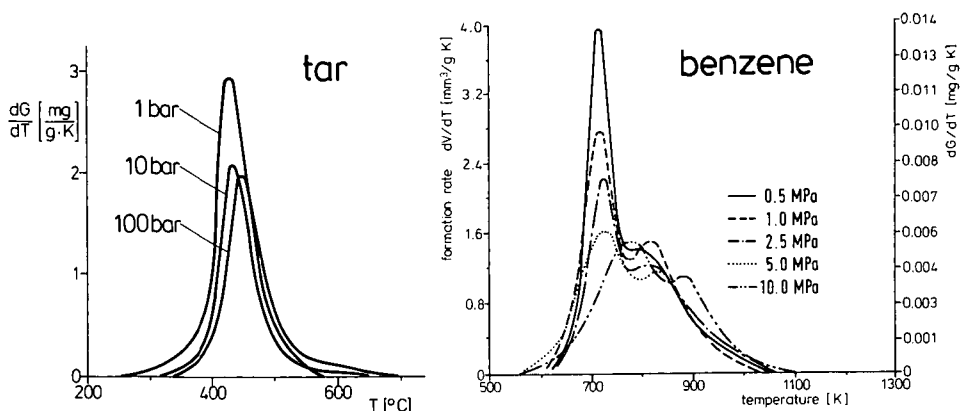


Fig. 4: Formation of liquid pyrolysis products depending on pressure (coal: 38,6 % V.M.; under  $N_2$ ; 3 K/min)

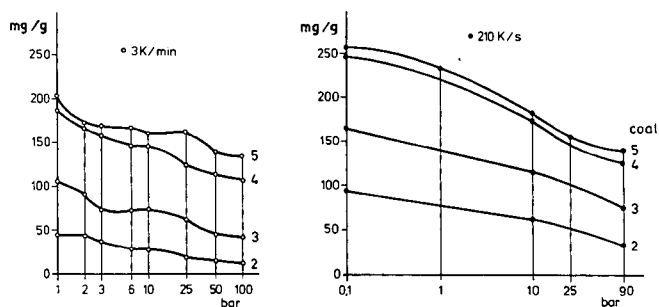


Fig. 5: Influence of pressure and rate of heating on tar yield for coals at different rank (coal 2: 16,2 % V.M.; 3: 23 %; 4: 32,9 %; 5: 36,3 %)

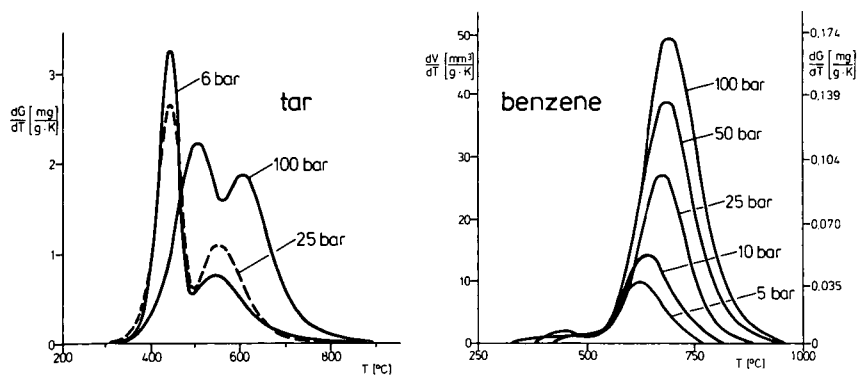


Fig. 6: Formation of liquid products during hydropyrolysis depending on pressure (coal: 38,6 % V.M.; 3 K/min)

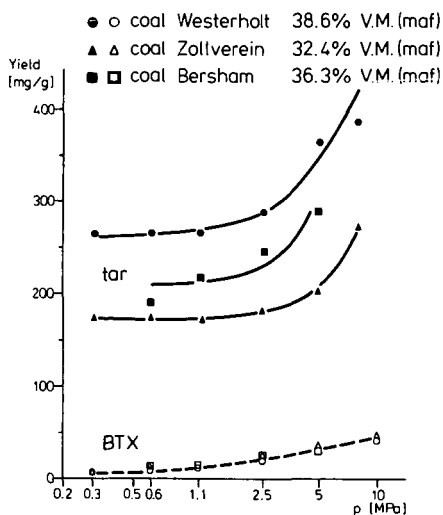


Fig. 7: Yield of BTX aromatics and tar from hydro-pyrolysis

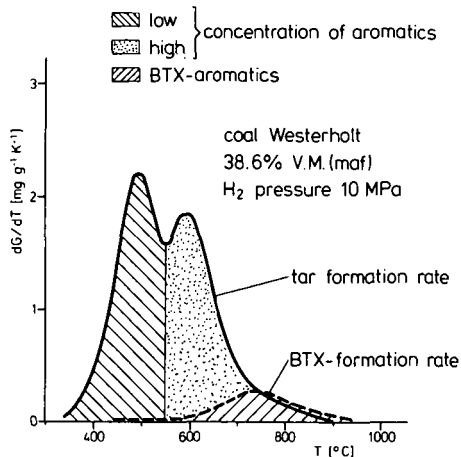


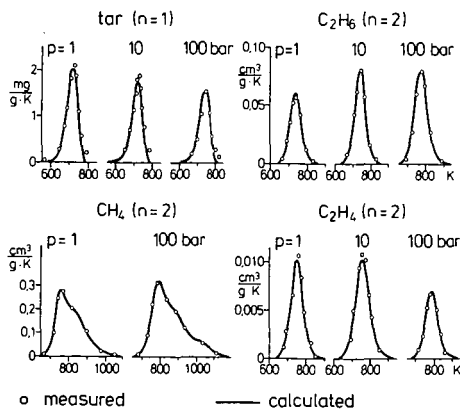
Fig. 8: Change of the contents of aromatics in the tar from hydro-pyrolysis

$$\begin{aligned}
 -\frac{dc}{dt} &= k \cdot c^n \\
 c &= a \cdot (V_0 - V) \\
 c_0 &= a \cdot V_0 \\
 \frac{dV}{dt} &= m = \text{const.} \\
 k &= k_0 \exp\left(-\frac{E}{RT}\right)
 \end{aligned}$$

Integration	
$n=1$	$\frac{dV}{dt} = \frac{k_0 \cdot V_0}{m} \exp\left[-\frac{E}{RT} - \frac{k_0}{m} I(T)\right]$
$n \neq 1$	$\frac{dV}{dt} = \frac{k_0}{m} \exp\left(-\frac{E}{RT}\right) \left[V_0^{1-n} + (n-1) \frac{k_0}{m} I(T)\right]^{\frac{n}{1-n}}$

with  $I(T) = \int_0^T \exp\left(-\frac{E}{RT}\right) dT$

Fig. 9: Kinetic equations and description of product formation curves for pyrolysis (coal: 32,9 % V.M.; N<sub>2</sub>; 3 K/min)



I. Thermal activation -fast-	$\begin{array}{c} R_i \\   \\ R_j - C - R_k \\   \\ \text{---} \end{array} \rightleftharpoons \begin{array}{c} R_i \\   \\ R_j - C^* - R_k \\   \\ \text{---} \end{array}$
II. Breaking of chemical bonds -slow-	$\begin{array}{c} R_i \\   \\ R_j - C - R_k \\   \\ \text{---} \end{array} \xrightarrow{k_{II}} \begin{array}{c} R_i \\   \\ R_j - C^\bullet - R_k \\   \\ \text{---} \end{array} + R_j^\bullet$
Formation of stable molecules	<div data-bbox="378 510 530 614">           a. Rearrangement with and without dissociation -fast-         </div> <div data-bbox="609 545 822 579"> <math display="block">R_j^\bullet \longrightarrow R_l + R_n^\bullet</math> </div> <div data-bbox="378 631 530 718">           b. Intermolecular radical reactions -fast-         </div> <div data-bbox="564 631 810 701">           e.g. dimerisation  <math display="block">R_j^\bullet + R_m^\bullet \longrightarrow R_j - R_m</math> </div>
by	<div data-bbox="378 753 508 822">           c. Transfer of radicals -slow         </div> <div data-bbox="564 753 833 822"> <math display="block">\begin{array}{c} R_n \\   \\ R_l + R_j^\bullet - C - R_a \\   \\ \text{---} \end{array} \xrightarrow{k_{IIIc}} R_j - R_l + \begin{array}{c} R_n \\   \\ C^\bullet - R_o \\   \\ \text{---} \end{array}</math> </div>

Fig. 10: Steps of the primary reaction during coal pyrolysis

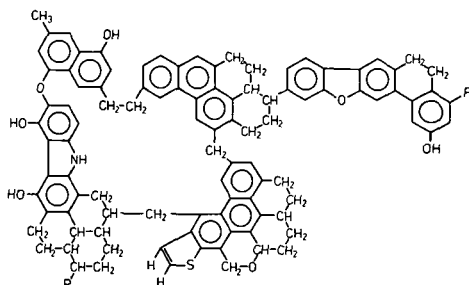


Fig. 11: Model molecule of a high volatile bituminous coal /14/